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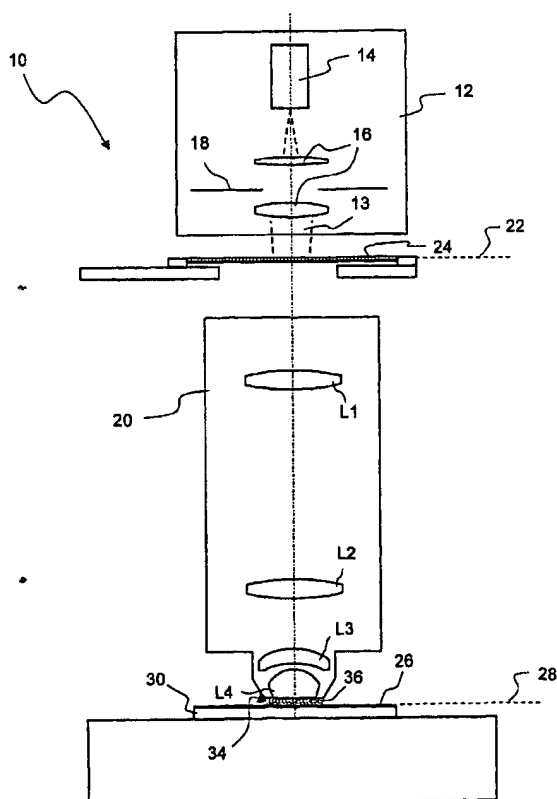
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(54) Title: MICROLITHOGRAPHIC PROJECTION EXPOSURE APPARATUS AND IMMERSION LIQUID THEREFORE



(57) Abstract: An immersion liquid for a microlithographic projection exposure apparatus is enriched with heavy isotopes. This reduces the chemical reactivity, which leads to an extension of the lifetime of optical elements which come in contact with the immersion liquid. For example, heavy water (D₂O), deuterated sulfuric acid, (D₂SO₄) or deuterated phosphoric acid D₃P¹⁶O₄ may be used. Organic compounds such as perfluoro polyethers, which have been deuterated or enriched with heavy oxygen (¹⁸O), are furthermore suitable.



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MICROLITHOGRAPHIC PROJECTION EXPOSURE APPARATUS AND IM- MERSION LIQUID THEREFORE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to microlithographic projection exposure apparatuses, such as those used for the production of microstructured components. The invention relates in particular to projection exposure apparatuses which have a projection lens designed for immersed operation, and to an immersion liquid suitable therefore.

2. Description of the Prior Art

Integrated electrical circuits and other microstructured components are conventionally produced by applying a plurality of structured layers to a suitable substrate which, for example, may be a silicon wafer. In order to structure the layers, they are first covered with a photoresist which is sensitive to light of a particular wavelength range, for example light in the deep ultraviolet (DUV) spectral range. The wafer coated in this way is subsequently exposed in a projection exposure apparatus. A pattern of diffracting structures, which is arranged on a mask, is projected onto the photoresist with the aid of a projection lens. Since the imaging scale is generally

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less than 1, such projection lenses are also often referred to as reduction objectives.

After the photoresist has been developed, the wafer is subjected to an etching process so that the layer becomes structured according to the pattern on the mask. The remaining photoresist is then removed from the other parts of the layer. This process is repeated until all the layers have been applied to the wafer.

One of the essential aims in the development of projection exposure apparatuses used for production is to be able to lithographically define structures with smaller and smaller dimensions on the wafer. Small structures lead to high integration densities, and this generally has a favorable effect on the performance of the microstructured components produced with the aid of such systems.

The size of the structures which can be defined depends primarily on the resolution of the projection lens. Since the resolution of the projection lenses is proportional to the wavelength of the projection light, one way of decreasing the resolution is to use projection light with shorter and shorter wavelengths. The shortest wavelengths used at present are in the deep ultraviolet (DUV) spectral range, namely 193 nm and 157 nm.

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Another way of decreasing the resolution is based on the idea of introducing an immersion liquid with a high refractive index into an intermediate space which remains between a last lens on the image side of the projection lens and the photoresist. Projection lenses which are designed for immersed operation, and which are therefore also referred to as immersion lenses, can achieve numerical apertures of more than 1, for example 1.3 or 1.4. The immersion, moreover, not only allows high numerical apertures and therefore improved resolution but also has a favorable effect on the depth of focus. The greater the depth of focus is, the less stringent are the requirements for exact axial positioning of the wafer in the image plane of the projection lens.

In the past, various fluorinated carbon compounds and highly pure water have predominantly been studied as immersion liquids. Although fluorinated carbon compounds often have a higher refractive index than water, the transmission for short-wave projection light is nevertheless greater with highly pure water. High purity of the water is necessary since even small amounts of impurities detrimentally reduce the transmission.

On the other hand, high purity of the water constitutes a great problem for the durability of the surfaces next to it, that is to say the last surface on the image side of the projection lens and the photosensitive layer. This is because highly pure water has a high reactivity and will

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start to dissolve those optical materials which are used for the production of transparent optical elements in view of their high transmission at very short wavelengths. These materials are primarily calcium fluoride, lithium
5 fluoride and barium fluoride. Although the solubility of these crystals with respect to highly pure water is relatively low in absolute terms, even material erosion of just a few nanometers is enough to degrade the optical imaging noticeably.

10 Besides this, highly pure water may also chemically modify the photosensitive layer. Admittedly, it would seem quite possible to develop photosensitive layers which are not significantly affected by highly pure water. Nevertheless, it is likely that such layers would have other
15 disadvantages such as lower photosensitivity or a less sharp exposure threshold.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an immersion liquid for a microlithographic projection exposure appa-
20 ratus, which is also highly transparent for short-wave projection light but has little chemical effect on materials which come in contact with the immersion liquid.

This object is achieved by an immersion liquid which is enriched with heavy isotopes.

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The invention is based on the discovery that the chemical reactivity of compounds is generally reduced when individual atoms are replaced by heavier isotopes. Chemical reactions therefore take place more slowly with compounds which are enriched with heavy isotopes. For the immersion liquid, this means that the materials coming in contact with it are affected less strongly compared with unenriched immersion liquids. The reduced chemical reactivity is attributable to the different thermal occupancy of the mass-dependent energy levels, that is to say quantum effects. The differences in the reaction rates are therefore temperature-dependent.

The term "isotopes" refers to atoms with the same atomic number, belonging to a given element, which contain different numbers of neutrons and therefore have different masses. With all elements for which there are isotopes, there is a natural isotope distribution that indicates which isotopes occur with which frequency in nature. For example, 99.762% of naturally occurring oxygen consists of the isotope ^{16}O , 0.038% of the isotope ^{17}O and 0.20% of the isotope ^{18}O . This isotope distribution is also encountered in oxygen compounds. In the present case, a liquid will generally be referred to as enriched with heavy isotopes if, starting with the natural isotope distribution, a single atom has been replaced by a heavier isotope. With reference to the example of oxygen, for instance, this could mean that the natural isotope distribution has been shifted by 1 per thousand from the iso-

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tope ^{16}O in favor of the heavier isotope ^{17}O , that is to say the compounds contain only 99.662% instead of 99.762% of the isotope ^{16}O , whereas they contain 0.138% (rather than 0.038%) of the isotope ^{17}O .

- 5 In order for the reduced reactivity to be noticeable at all, the proportion of at least one heavy isotope should be at least doubled, and preferably at least one hundred times greater, in comparison with the natural isotope distribution.
- 10 The relative mass change between different isotopes is comparatively small for heavier elements, which in this context also include oxygen. In heavier elements, therefore, the isotopes differ only little with respect to their chemical properties and therefore with respect to
- 15 their reactivity. Enrichment of immersion liquids with the isotopes of heavier elements, such as oxygen, therefore leads to only a comparatively small reduction in the reactivity.

Isotopes of elements with a low atomic number, however,

20 may differ greatly with respect to their chemical properties. These differences are particularly significant for hydrogen, which contains only one proton. There are three isotopes of hydrogen, namely the light hydrogen ^1H also referred to as protium, the heavy hydrogen ^2H usually re-

25 ferred to as deuterium D, which contains one proton and one neutron, and superheavy hydrogen ^3H , which contains

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one proton and two neutrons and is also referred to as tritium T. Since the masses of the three hydrogen isotopes are in the proportion 1:2:3, the percentage mass difference between the isotopes is large.

5 The natural isotope distribution of hydrogen is 99.9855% for light hydrogen, 0.0145% for deuterium and $10^{-15}\%$ for tritium. If all the molecules in a liquid contain hydrogen, and if more than 2% of these molecules in turn contain deuterium, then this corresponds to enrichment by
10 more than 100 times in comparison with the natural isotope distribution.

Yet the higher reaction inertia of deuterium is not yet very noticeable even with such enrichment, since the chemical properties are still dominated by the 98% of the
15 molecules which contain not deuterium but light hydrogen. Preferably more than 80% and, more preferably, more than 99% of the molecules contained in the immersion liquid should therefore contain deuterium instead of hydrogen.

The relatively low reactivity of deuterium compounds in
20 comparison with compounds that contain light hydrogen becomes noticeable primarily when the hydrogen content in the immersion liquid is relatively high overall. This applies to water, for example, since two hydrogen atoms occur on each oxygen atom. Water which is deuterated to a
25 high degree is generally referred to as heavy water (D_2O) and is produced on an industrial scale. If virtually all

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of an immersion liquid consists of heavy water (that is to say more than 99 molar per cent) then it will have a significantly reduced reactivity in comparison with normal water, that is to say water with a natural isotope
5 distribution. The lifetime of sensitive optical materials, for example calcium fluoride crystals, can thereby be extended by a factor of about 5 or more. This presents significant cost advantages, since such optical materials are very expensive. Furthermore, replacement of the optical
10 elements in question leads to prolonged down-times of the projection exposure apparatuses and therefore to production losses.

Besides D_2O , heavy water may also contain substantial amounts of DHO which likewise has a reduced reactivity in
15 comparison with normal water (H_2O). An extra reduction in the reactivity can be achieved if at least some of the oxygen is also replaced by the heavier oxygen isotope ^{18}O .

If heavy water is used as the immersion liquid, then the projection exposure apparatus may contain a thermal regulating
20 device by which the immersion liquid can be brought to a setpoint temperature, which is at least approximately equal to the temperature at which heavy water has its maximum refractive index for a given ambient pressure. The refractive index of liquids generally depends
25 on their temperature and the wavelength of the light passing through the liquid. Minor temperature fluctuations, as may occur owing to the energetic projection

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light as it passes through the immersion liquid or owing to coldness of evaporation, cause local refractive index fluctuations via this dependency. These in turn lead to striation of the immersion liquid and therefore possibly to serious impairment of the imaging quality of the projection lens.

But if the immersion liquid is kept to a temperature at which heavy water has its maximum refractive index, then temperature fluctuations will only lead to very small differences in the optical path length. It is advantageous to use heavy water in this context because heavy water reaches its maximum refractive index at a relatively high temperature, which is about 11.28°C at an ambient pressure of 1 bar and a wavelength of $\lambda = 589$ nm. Conversely, this temperature is about -0.4°C for normal water under the said conditions, and therefore below the freezing point.

In view of the temperature dependency, moreover, it is advantageous to use heavy water as the immersion liquid even if the setpoint temperature adjusted by the thermal regulating device lies significantly above the temperature interval, between about 10°C and 13°C, containing the temperature at which the maximum refractive index is reached for the conventionally used wavelengths and the normally prevailing ambient pressures. If the immersion liquid is at the temperature of 22°C normally prevailing in most microlithographic projection exposure apparatuses,

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for example, then the temperature dependency will be reduced by about a factor of 2 in comparison with light water; the exact value of the factor depends inter alia on the wavelength of the projection light.

- 5 The reduced temperature dependency of the refractive index of heavy water makes it possible to significantly increase the thickness of the immersion layer, but without the stronger heating leading to a significant impairment of the imaging properties. The minimum distance between
10 the last optical surface on the image side and a photo-sensitive layer to be exposed, which hitherto has usually been 2 mm, may now be more than 2.5 mm, for example, or even more than 5 mm.

Owing to the reduced temperature dependency of the refractive index, furthermore, the projection lens can be
15 designed so that the immersion liquid is convexly curved towards an object plane of the projection lens during immersed operation. This can be achieved, for example, if the immersion liquid is directly adjacent to a concavely
20 curved surface on the image side of the last optical element on the image side during immersed operation. This provides a kind of "liquid lens", the advantage of which is primarily that it is very cost-effective. A calcium fluoride crystal, which is very expensive, has hitherto
25 mainly been used as a material for the last imaging optical element on the image side in projection exposure apparatuses which are designed for wavelengths of 193 nm.

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The calcium fluoride crystal becomes gradually degraded owing to the high radiation intensities which occur in this last imaging optical element on the image side, which in the end makes it necessary to change it.

5 If this crystal is "replaced" by heavy water, a fact which must of course be taken into account when configuring the projection lens, then this leads to a substantially more cost-effective solution. Although the optical paths of the projection light in such a heavy-water "liquid lens" are comparatively long, and more heat is there-
10 fore produced owing to absorption, the refractive index remains relatively constant owing to the low temperature dependency of heavy water.

A protective plate which seals the liquid lens at the
15 bottom, and which may for example consist of LiF, may also be arranged between such a liquid lens and a photosensitive layer to be exposed.

The immersion liquid may contain both light and heavy water, or it may consist of only one of these two components. Even with a mixing ratio of 1:1, the immersion
20 liquid has a significantly reduced reactivity in comparison with highly pure normal water.

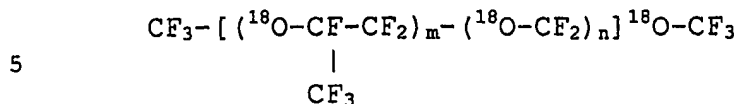
Another compound with a high hydrogen content which is suitable as an immersion liquid is sulfuric acid H_2SO_4 .
25 Deuterated sulfuric acid D_2SO_4 is substantially more

chemically inert than normal sulfuric acid H_2SO_4 , and it also has the advantage of a refractive index which is about 30% higher in comparison with water. A further reduction in the reactivity can be achieved if the heavier isotope ^{17}O , or in particular ^{18}O , is used instead of the oxygen isotope ^{16}O . In the latter case, the immersion liquid contains significant amounts of $\text{D}_2\text{S}^{18}\text{O}_4$.

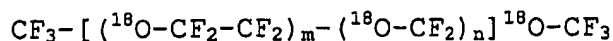
An even smaller chemical reactivity and a higher refractive index may be achieved if the immersion liquid contains deuterated phosphoric acid $\text{D}_3\text{P}^{16}\text{O}_4$. For example, a 15% deuterated phosphoric acid solution has a refractive index of 1.65. A further reduction in the reactivity can be achieved if the heavier isotope ^{17}O , or in particular ^{18}O , is used instead of the oxygen isotope ^{16}O , yielding $\text{D}_3\text{P}^{17}\text{O}_4$ or $\text{D}_3\text{P}^{18}\text{O}_4$. Of course, the solution may contain heavy water as well. The smallest chemical reactivity is thus achieved with an aqueous solution of $\text{D}_3\text{P}^{18}\text{O}_4 \cdot \text{D}_2\text{O}$ although even the less enriched $\text{D}_3\text{P}^{16}\text{O}_4 \cdot \text{H}_2\text{O}$ has still a very low chemical reactivity.

Enrichment with heavier isotopes is also possible for organic immersion liquids, where it likewise leads to a reduced reactivity. Organic immersion liquids which are particularly suitable for being enriched with the oxygen isotope ^{18}O are described in US 2002/0163629 A1, the content of which is fully incorporated into the subject-matter of the present application. These are various perfluoro polyethers (PFPE) which are available under the

brand names Fomblin Y®, Fomblin Z® and Demnum™. The perfluoro polyethers enriched with the heavy oxygen isotope ¹⁸O can be described by the following chemical formulae:

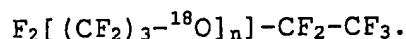


with $m+n = 8$ to 45 and m/n 20 to 1000 ;

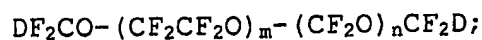
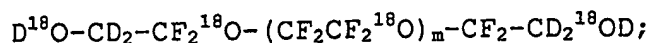
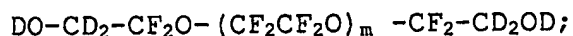


with $m+n = 40$ to 180 and m/n 0.5 to 2

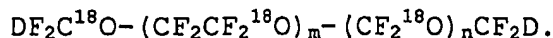
and



Examples of other organic immersion liquids which have high refractive indices and reduced chemical reactivity when deuterated and/or enriched with the oxygen isotope ¹⁸O, and which are therefore suitable as immersion liquids, are the heavy perfluoro polyethers listed below:



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$\text{CF}_3(^{18}\text{OCF}_2\text{CF}_2)_m-(^{18}\text{OCF}_2)_n-^{18}\text{OCF}_3$, and long-chained hydrocarbons in which at least 10% of the hydrogen is replaced by deuterium, have similar properties.

- 5 An organic immersion liquid should contain at least 1 molar per cent, but preferably more than 10 molar per cent and in particular more than 90 molar per cent of at least one of the organic compounds mentioned above by way of example.
- 10 An additional or alternative way of resolving the problem of chemically corrosive immersion liquids is to provide a projection lens in which the refractive index of the last surface on the image side is at least approximately the same as the refractive index of the immersion liquid. Al-
- 15 though this measure does not prevent the immersion liquid from chemically attacking a last surface on the image side of the projection lens, it does reduce the detrimental consequences for the imaging quality. This is because of the closer the ratio of the refractive indices of this
- 20 surface and of the immersion liquid lies to 1, the less is the refraction at the interface. If the refractive indices were exactly the same, then light would not be refracted at the interface and therefore the shape of the interface would actually have no effect on the beam path.
- 25 Local deformations on the surface, due to the immersion liquid, could not then affect the imaging quality.

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No material pairings of solid and liquid substances are yet known which are suitable respectively as a lens material and as an immersion liquid, and which have exactly the same refractive index. There are, however, material pairings in which the refractive indices of the immersion liquid and of the solid material next to it are so close to each other that the ratio of the two refractive indices differs from 1 by no more than 5%, or even by no more than 1%.

For example, if a thin layer of MgF_2 is vapour-deposited on a last surface on the image side and light water, heavy water or a mixture of the two liquids is used as the immersion liquid, then with particularly compact MgF_2 the said value may readily be less than 1%. Applying a layer by vapour deposition on the last surface on the image side has, inter alia, the advantage that arbitrarily curved layers can be produced very easily in this way.

The last optical element on the image side may moreover consist entirely of a suitable material. An example of a suitable material for this element, which may for example be a planoconvex lens or a plane-parallel plate, is lithium fluoride (LiF). At a wavelength of 193 nm, LiF has a refractive index of 1.4432 whereas the refractive index of light water (H_2O) is 1.4366 and the refractive index of heavy water (D_2O) is 1.4318. Here again, the ratio of the two refractive indices differs from 1 by less than 1% with all mixing ratios.

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Another alternative or additional way of resolving the problem with the chemical reactivity of the immersion liquid is to supplement an immersion liquid, initially consisting of highly pure water, with an accurately established amount of at least one additive that is transparent for the projection light used in the projection exposure apparatus. Owing to the incorporation of additives, the water is no longer highly pure and therefore much less reactive. If additives which are also highly transparent for the projection light wavelength being used, when they are in the dissociated state, are added in a controlled way then it is possible to achieve a transparency which is only insubstantially less than that of highly pure water. Examples of additives suitable for this are LiF, NaF, CaF₂ or MgF₂. The highly pure water used as the starting-material may in this case consist of light water, heavy water or a mixture of light and heavy water.

Experiments have shown that even relatively low ion concentrations in the water are sufficient to significantly reduce its chemical reactivity. In particular, it has been found that the at least one additive should dissociate in the immersion liquid so that the electrical conductivity of the immersion liquid is between about 4×10^{-8} S/m and about 4×10^{-6} S/m, and particularly preferable between about 3.5×10^{-8} S/m and about 6×10^{-7} S/m, after adding the additive.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages and features of the invention will be found in the following description of the exemplary embodiments, with reference to the drawings in which:

- 5 Figure 1 shows a meridian section through a projection exposure apparatus according to a first exemplary embodiment of the invention, in a highly simplified schematic representation which is not true to scale;
- 10 Figure 2 shows an enlarged detail of the end on the image side of a projection lens, which is part of the projection exposure apparatus as shown in Figure 1;
- 15 Figure 3 shows a representation corresponding to Figure 2, according to a second exemplary embodiment in which a layer of MgF_2 is vapour-deposited on a last lens on the image side of the projection lens;
- 20 Figure 4 shows a detail on the image side of the projection exposure apparatus as shown in Figure 1, according to a third exemplary embodiment in which a thermal regulating device is provided for adjusting the temperature of the immersion liquid;

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Figure 5 shows a graph plotting the temperature dependency of the refractive indices of light and heavy water and mixtures thereof;

Figure 6 shows an enlarged detail of the end on the image side of another projection lens, in which the last optical element on the image side is a deuterated sulfuric-acid liquid lens;

Figure 7 shows the projection lens of Figure 6, in which the liquid lens is sealed by a plate on the image side.

DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1 shows a meridian section through a microlithographic projection exposure apparatus, denoted overall by 10, according to a first exemplary embodiment of the invention in a highly simplified schematic representation. The projection exposure apparatus 10 has an illumination device 12 for the generation of projection light 13, which inter alia comprises a light source 14, illumination optics indicated by 16 and a diaphragm 18. In the exemplary embodiment which is represented, the projection light has a wavelength of 193 nm.

The projection exposure apparatus 10 furthermore includes a projection lens 20 which contains a multiplicity of lens elements, only some of which denoted by L1 to L4 are

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represented by way of example in Figure 1 for the sake of clarity. The projection lens 20 is used to project a reduced image of a reticle 24, which is arranged in an object plane 22 of the projection lens 20, onto a photosensitive layer 26 which is arranged in an image plane 28 of the projection lens 20 and is applied to a support 30. The photosensitive layer may, for example, be a photoresist which becomes chemically modified when it is exposed to projection light with a particular intensity.

10 In the exemplary embodiment which is represented, the last lens element L4 on the image side is a high-aperture, comparatively thick convexoplane lens element which is made of a calcium fluoride crystal. The term "lens element", however, is in this case also intended to include
15 a plane-parallel plate. As can be seen particularly clearly from the enlarged representation in Figure 2, a plane surface 32 on the image side of the lens element L4 together with the photosensitive layer 26 lying opposite delimits an intermediate space 34 in a vertical direction,
20 which is filled with an immersion liquid 36. With an appropriate layout of the projection lens 20, the immersion liquid 36 makes it possible to increase its numerical aperture in comparison with a dry objective and/or improve the depth of focus. Since immersion objectives for micro-
25 lithography projection exposure apparatuses to this extent are known, further details will not be explained in this regard.

- 20 -

In the exemplary embodiment which is represented, the immersion liquid 36 consists of highly pure heavy water (D_2O). The purity of the heavy water is more than 99 molar per cent. This means that out of 100 water molecules, at most 1 molecule is not a D_2O molecule. The remaining molecules are either H_2O molecules or HDO molecules. The proportion of molecules other than those mentioned should be as low as possible, and should optimally not exceed 0.1 molar per cent.

10 The heavy water used as the immersion liquid 36 has the property that, while having a similarly high transparency, it exhibits a comparatively low reactivity in comparison with highly pure light water. The calcium fluoride crystal forming the adjacent lens element L4 is therefore affected substantially less by the immersion liquid 36 than by highly pure water. Only to a minor extent, therefore, will the individual crystal layers be dissolved and gradually lead to a deformation of the originally plane last surface 32 on the image side.

20 The second exemplary embodiment as shown in Figure 3 differs from the exemplary embodiment represented in Figures 1 and 2, on the one hand, in that a layer 38 of magnesium fluoride (MgF_2) - represented with an exaggerated thickness in Figure 3 - is vapour-deposited on the plane surface of the last lens element L4 on the image side.

Highly compact magnesium fluoride has a refractive index of merely 1.4345 at a wavelength of 193 nm. At a wave-

length of 193 nm, the refractive index of the layer 38 is therefore significantly closer to the refractive index $n_{D20} = 1.4318$ of the heavy water than the refractive index $n_{CaF2} = 1.5014$ of calcium fluoride, which forms the lens element L4. If the heavy water attacks the layer 38, then this will indeed lead to deformation of the surface of the layer 38 that comes in contact with the water. But owing to the similar refractive indices, the refractive index ratio at this interface is so small that the surface deformations generated in the layer 38 by the immersion liquid 36 have scarcely any optical effect.

The layer 38 may also consist of another resistant material with a low refractive index. It need not necessarily be vapour-deposited, however, but may also be applied to the plane surface 32 of the layer L4 in a different way. For example, it is also conceivable to use a self-supporting thin plate of lithium fluoride (LiF) which is bonded to the plane surface 32 of the lens element L4. The refractive index of lithium fluoride is 1.4432 at a wavelength of 193 nm. In comparison with the refractive indices of light and heavy water, the refractive index of LiF is therefore about 5% to 8% higher.

The second exemplary embodiment according to Figure 3 also differs from the first exemplary embodiment, as represented in Figures 1 and 2, in that small amounts of additives are also mixed with the heavy water which is used as the immersion liquid 36. In this way, the reactivity

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of the immersion liquid 36 is significantly reduced further. The additives are selected according to the criterion that they absorb as little as possible of the projection light being used. In this regard, examples of
5 suitable additives are lithium fluoride (LiF), sodium fluoride (NaF), calcium fluoride (CaF₂) and magnesium fluoride (MgF₂). The dissociated ions of these substances reduce the chemical activity of the immersion liquid 36, but without significantly compromising its high transmissi-
10 on capacity.

Figure 4 shows a detail on the image side of a projection exposure apparatus according to a third exemplary embodiment. Here, the support 30 is fastened on the bottom of a container 42 which is in the shape of a trough and is
15 open at the top. The container 42 is filled sufficiently with the immersion liquid 36 for the projection lens 20 to be immersed, with its last surface 32 on the image side in the immersion liquid, during operation of the projection exposure apparatus.

20 Via a feed line 46 and a discharge line 47, the container 42 is connected to a treatment unit 48 which contains a circulating pump, a filter for purifying the immersion liquid 36 and a thermal regulating device 50, in a manner which is known per se and is therefore not represented in
25 detail. Further details may, for example, be found in US 4 346 164 A, the disclosure of which is fully incorporated into the subject-matter of the present application.

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The treatment unit 48, the feed line 46, the discharge line 47 and the container 42 form an immersion device, denoted overall by 52, in which the immersion liquid 36 circulates while being purified and kept at a constant
5 temperature.

In the exemplary embodiment shown in Figure 4, approximately 100% of the immersion liquid 36 consists of heavy water D₂O. The thermal regulating instrument 50 is connected, in a manner which is not represented in detail,
10 to a temperature sensor which measures the temperature of the immersion liquid 36 in the intermediate space 34. Regulation is used to ensure that the temperature in the intermediate space 34 is about 11.3°C. This corresponds approximately to the temperature at which heavy water has
15 its maximum refractive index with an ambient pressure of 1 bar and the wavelength of 589.3 nm used in this exemplary embodiment. The temperature adjustment may be relatively imprecise here, since with this configuration the temperature fluctuations have no effect, or no significant
20 effect, on the refractive index of the immersion liquid 36.

This will be explained below with reference to Figure 5, which shows a graph on which the refractive index n is plotted for light water, heavy water and mixtures of
25 light and heavy water in different mixing ratios, as a function of the temperature T . The refractive index was in this case determined for a wavelength of 589.3 nm. It

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can be seen from the graph that light water (H_2O) has its maximum refractive index for this wavelength and at a temperature of about $-0.4^\circ C$. From there, to a first approximation, the refractive index decreases quadratically as the temperature falls or rises. The projection exposure apparatus cannot be operated at such a low temperature.

With heavy water (D_2O), however, the maximum refractive index is found at a temperature of about $11.28^\circ C$. Here again, the decrease in the refractive index towards lower or higher temperatures is likewise quadratic to a first approximation. If the thermal regulating device 50 adjusts the temperature exactly to the value at which the maximum refractive index is reached, then the temperature dependency dn/dT of the refractive index n will be equal to zero. This temperature is therefore the optimum working point for the projection exposure apparatus since minor temperature fluctuations, as may occur owing to the energetic projection light 13 or coldness of evaporation at the surface of the immersion liquid 36, do not alter the refractive index of the immersion liquid 36 and therefore the imaging properties of the projection lens 20. The immersion liquid 36 then has a constant refractive index throughout the intermediate space 34.

In mixtures of light and heavy water, the temperature at which the refractive index of the mixture in question has its maximum decreases as the proportion of water in-

- 25 -

creases. This is indicated by a dashed line 58 in Figure 5.

It is furthermore clear from Figure 5 that even at a temperature of 22°C, which is the temperature usually set in projection exposure apparatuses, the temperature dependency of heavy water is much less than the temperature dependency of light water. In fact, with an ambient pressure of 1 bar and a temperature of 22°C, the temperature dependency of the refractive index n for light water $dn/dT = 96.8 \cdot 10^{-6} \text{ 1/K}$, whereas for heavy water just $dn/dT = 41.1 \cdot 10^{-6} \text{ 1/K}$, that is to say approximately half as much as for light water. Even above the optimum athermal working point of about 11°C, a significantly reduced temperature dependency of the refractive index is therefore achieved when heavy water is used. This in turn allows improved imaging and/or higher scanning rates.

Towards shorter wavelengths, the temperature dependencies dn/dT at a given temperature firstly increase, until they reach their maximum at a wavelength of about 250 nm. At even shorter wavelengths, the temperature dependency of the refractive indices decreases again. At a wavelength of 193 nm, the temperature dependency dn/dT for light water at the temperature of 22°C is about $100 \cdot 10^{-6} \text{ 1/K}$, which corresponds approximately to the value at a wavelength of 589.3 nm.

Figure 6 shows an enlarged detail of an end on the image side of a projection lens denoted by 120, according to another exemplary embodiment in which the lens element L4 is designed as a convexoconcave meniscus lens. The immersion liquid 34, approximately 100% of which consists of deuterated sulfuric acid D_2SO_4 in this case, extends up to the concave surface 40 of the lens element L4 and is itself therefore convexly curved on the object side. The resulting "liquid lens" has the advantage, inter alia, that it can withstand heavy radiation loads particularly well in the vicinity of the end on the image side and, furthermore, it can be changed in a comparatively straightforward and cost-effective way. In this context, it should also be noted that the surrounding atmosphere ought to be as free of water as possible, since highly pure sulfuric acid is strongly hygroscopic even when it is deuterated.

An even smaller chemical reactivity and higher refractive indices may be achieved if the immersion liquid 34 contains deuterated phosphoric acid $D_3P^{16}O_4$ that may be further enriched with heavy isotopes, thus yielding $D_3P^{17}O_4$ or $D_3P^{18}O_4$.

In order to obtain $D_3P^{16}O_4$ or $D_3P^{18}O_4$, the following method may be used: Highly pure phosphor is oxidized with oxygen ^{16}O or ^{18}O which results in $P_2^{16}O_5$ or $P_2^{18}O_5$, respectively. When adding heavy water D_2O , an aqueous solution is obtained whose acidity may be controlled by volatilizing or by

adding more heavy water. The refractive index of the solution increases and the transmission decreases with growing acidity. This means that for higher refractive indices the thickness of the intermediate space 34 should
5 be reduced.

The smallest chemical reactivity is achieved with an aqueous solution of $D_3P^{18}O_4 \cdot D_2O$ although even the less enriched $D_3P^{16}O_4 \cdot H_2O$ has still a very low chemical reactivity.

- 10 In order to prevent the immersion liquid 34 from being contaminated and flowing out of the cavity formed below the lens element L4, the liquid lens formed by the heavy water in the variant shown in Figure 7 is sealed on the image side by a plane-parallel plate 42 made of LiF.

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CLAIMS

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1. Microlithographic projection exposure apparatus hav-
ing a projection lens (20; 120) whose last optical
5 surface on the image side is immersed in an immersion
liquid (36),

characterized in that

the immersion liquid (36) is enriched with heavy isotopes.

2. Projection exposure apparatus according to Claim 1,
10 characterized in that the proportion of at least one
heavy isotope is at least doubled in comparison with the
natural isotope distribution.

3. Projection exposure apparatus according to Claim 1
or 2, characterized in that the immersion liquid (36)
15 is enriched with deuterium.

4. Projection exposure apparatus according to Claim 3,
characterized in that more than 1 per cent of the
molecules contained in the immersion liquid (36) contain
deuterium.

20 5. Projection exposure apparatus according to Claim 4,
characterized in that more than 80 per cent of the

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molecules contained in the immersion liquid (36) contain deuterium.

6. Projection exposure apparatus according to Claim 5,
characterized in that more than 99 per cent of the
5 molecules contained in the immersion liquid (36) contain deuterium.

7. Projection exposure apparatus according to Claim 6,
characterized in that more than 99 molar per cent of
the immersion liquid (36) consists of heavy water.

10 8. Projection exposure apparatus according to Claim 7,
characterized in that the projection exposure apparatus (10) contains a thermal regulating device (15) by
which the immersion liquid (36) can be brought to a set-
point temperature, which is at least approximately equal
15 to the temperature at which heavy water has its maximum refractive index for a given ambient pressure.

9. Projection exposure apparatus according to Claim 8,
characterized in that the temperature is between
about 7°C and about 16°C, and preferably between about
20 10°C and about 13°C.

10. Projection exposure apparatus according to Claim 8
or 9, characterized in that the projection lens (120)
is designed so that the immersion liquid (36) is convexly

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curved towards an object plane (22) of the projection lens (120) during immersed operation.

11. Projection exposure apparatus according to Claim 10,
characterized in that the immersion liquid (36) is
5 directly adjacent to a concavely curved surface (40) on
the image side of the last optical element (L4) on the
image side during immersed operation.

12. Projection exposure apparatus according to one of
Claims 8 to 11, characterized in that the minimum
10 distance between the last optical surface on the image
side and a photosensitive layer to be exposed is more
than 2.5 mm, preferably more than 5 mm.

13. Projection exposure apparatus according to one of
Claims 3 to 6, characterized in that the immersion
15 liquid (36) contains D_2SO_4 .

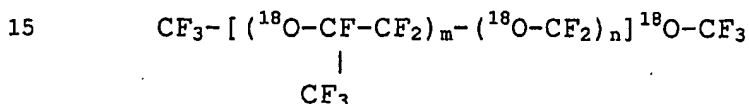
14. Projection exposure apparatus according to Claim 13,
characterized in that more than 10 per cent of the
molecules contained in the immersion liquid (36) contain
the oxygen isotope ^{18}O .

20 15. Projection exposure apparatus according to one of
Claims 3 to 6, characterized in that the immersion
liquid (36) contains D_3PO_4 .

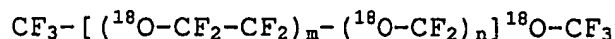
- 31 -

16. Projection exposure apparatus according to Claim 13, characterized in that more than 10 per cent of the molecules contained in the immersion liquid (36) contain the oxygen isotope ^{18}O .
- 5 17. Projection exposure apparatus according to one of Claims 13 to 16, characterized in that the immersion liquid is an aqueous solution containing D_2O .
18. Projection exposure apparatus according to one of Claims 13 to 17, characterized in that the immersion
10 liquid is an aqueous solution containing HDO .

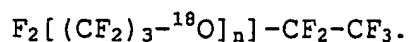
19. Projection exposure apparatus according to one of Claims 3 to 6, characterized in that the immersion liquid (36) contains at least 1 molar per cent of at least one of the three following perfluoro polyethers:



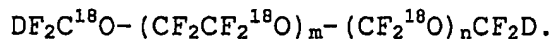
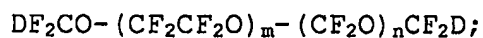
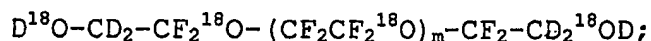
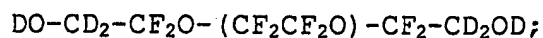
with $m+n = 8$ to 45 and m/n 20 to 1000 ;



20 with $m+n = 40$ to 180 and m/n 0.5 to 2 ;



20. Projection exposure apparatus according to one of Claims 3 to 6, characterized in that the immersion liquid (36) contains at least 1 molar per cent of at least one of the two following four heavy perfluoro poly-
5 ethers:



- 10 21. Projection exposure apparatus according to one of Claims 3 to 6, characterized in that the immersion liquid (36) contains at least 1 molar per cent of $\text{CF}_3(^{18}\text{OCF}_2\text{CF}_2)_m\text{-(}^{18}\text{OCF}_2)_n\text{-}^{18}\text{OCF}_3$.

22. Projection exposure apparatus according to one of
15 Claims 3 to 6, characterized in that the immersion liquid (36) contains long-chained heavy hydrocarbons in which at least 10% of the hydrogen is replaced by deuterium.

23. Projection exposure apparatus according to one of
20 the preceding claims, characterized in that the refractive index of the last surface (32) on the image side is at least approximately the same as the refractive

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is at least approximately the same as the refractive index of the immersion liquid (36).

24. Projection exposure apparatus according to Claim 23, characterized in that the ratio of the refractive indices of the immersion liquid (36) and of the surface (32) differs from 1 by no more than 10^{-1} , preferably no more than 10^{-2} .
25. Projection exposure apparatus according to Claim 23 or 24, characterized in that the surface (32) consists of LiF or MgF_2 .
26. Projection exposure apparatus according to one of Claims 23 to 25, characterized in that the last surface (32) on the image side is formed by a layer (36) applied by vapour deposition.
27. Projection exposure apparatus according to one of the preceding claims, characterized in that the immersion liquid (36) consists of highly pure water which is supplemented with an accurately established amount of at least one additive that is transparent for the projection light used in the projection exposure apparatus (10).
28. Projection exposure apparatus according to Claim 27, characterized in that the at least one additive dissociates in the immersion liquid (36) so that the electrical conductivity of the immersion liquid is between

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about 4×10^{-8} S/m and about 4×10^{-6} S/m, and particularly preferable between about 3.5×10^{-8} S/m and about 6×10^{-7} S/m, after adding the additive.

29. Projection exposure apparatus according to one of
5 Claims 27 or 28, characterized in that the highly pure water consists of light water and/or heavy water.

30. Projection exposure apparatus according to one of
Claims 27 to 29, characterized in that the at least one additive contains LiF, NaF, CaF_2 , SrF_2 or MgF_2 .

10 31. Microlithographic projection exposure apparatus having a projection lens (20; 120) whose last optical surface on the image side is immersed in an immersion liquid (36),

characterized in that

15 the refractive index of the immersion liquid (36) has a temperature dependency dn/dT which is less than 5×10^{-5} 1/K and, in particular, less than 1×10^{-5} 1/K.

32. Microlithographic projection exposure apparatus having a projection lens (20; 120) whose last optical
20 surface on the image side is immersed in an immersion liquid (36),

characterized in that

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the refractive index of the last surface (32) on the image side is at least approximately the same as the refractive index of the immersion liquid (36).

33. Microlithographic projection exposure apparatus having a projection lens (20; 120) whose last optical surface on the image side is immersed in an immersion liquid (36),

characterized in that

the immersion liquid (36) consists of highly pure water which is supplemented with an accurately established amount of at least one additive that is transparent for the projection light used in the projection exposure apparatus (10).

34. Immersion liquid for a microlithographic projection exposure apparatus,

characterized in that

the immersion liquid (36) is enriched with heavy isotopes.

35. Use of a liquid enriched with heavy isotopes as an immersion liquid (36) in a microlithographic projection exposure apparatus (10).

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36. Method for the microlithographic production of a microstructured component, having the following steps:

- a) providing a projection lens (20; 120);
 - 5 b) arranging a reticle (24), which contains structures to be projected, in an object plane (22) of the projection lens (20; 120);
 - c) introducing an immersion liquid (36) into an intermediate space (34) which remains between a last optical element (L4) on the image side of the projection lens (20; 120) and a photosensitive layer (26),
10 the immersion liquid (36) being enriched with heavy isotopes;
 - d) projecting the structures onto the photosensitive
15 layer (26).
37. Microstructured component, characterized in that it is produced by the method according to claim 36.

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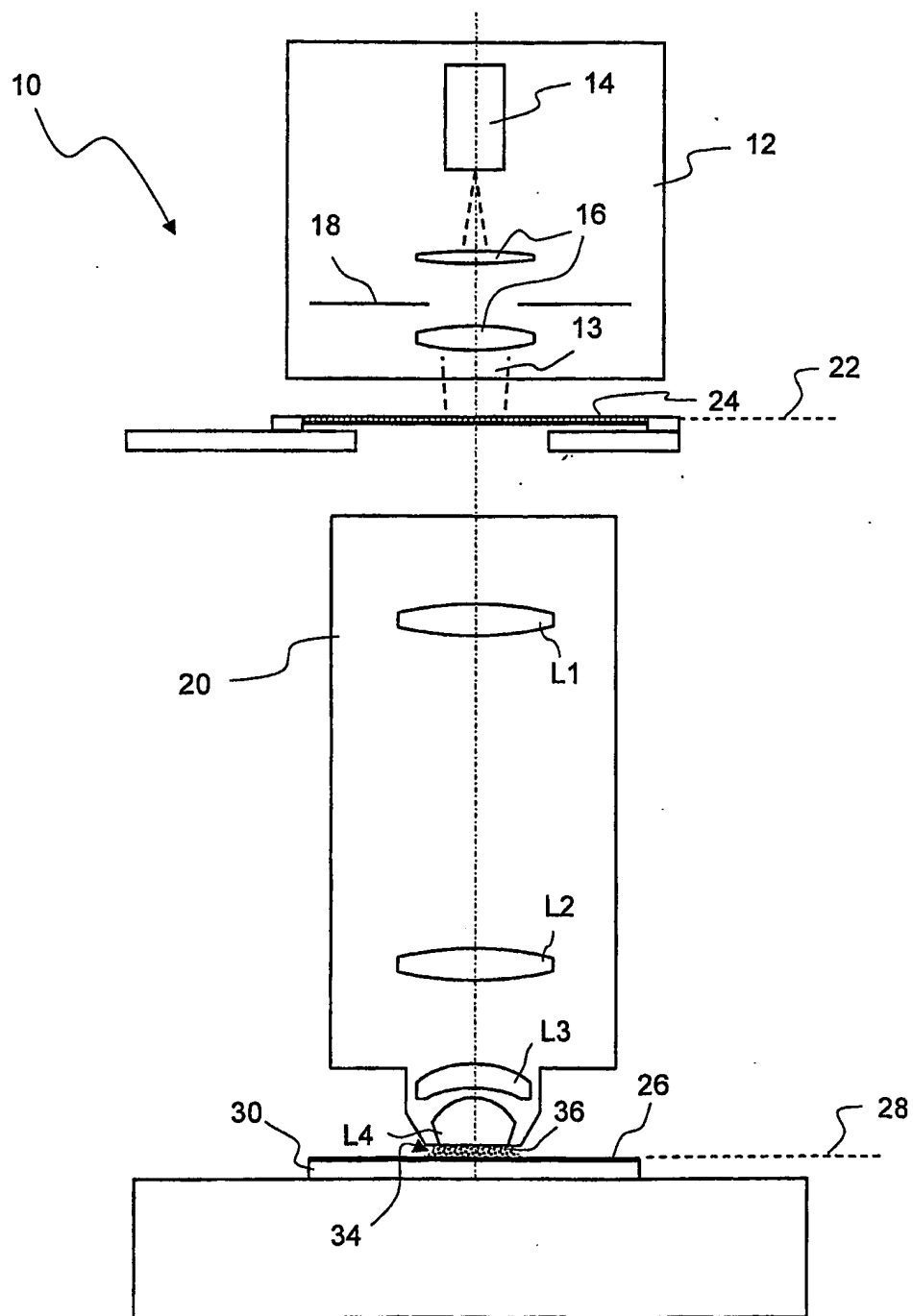
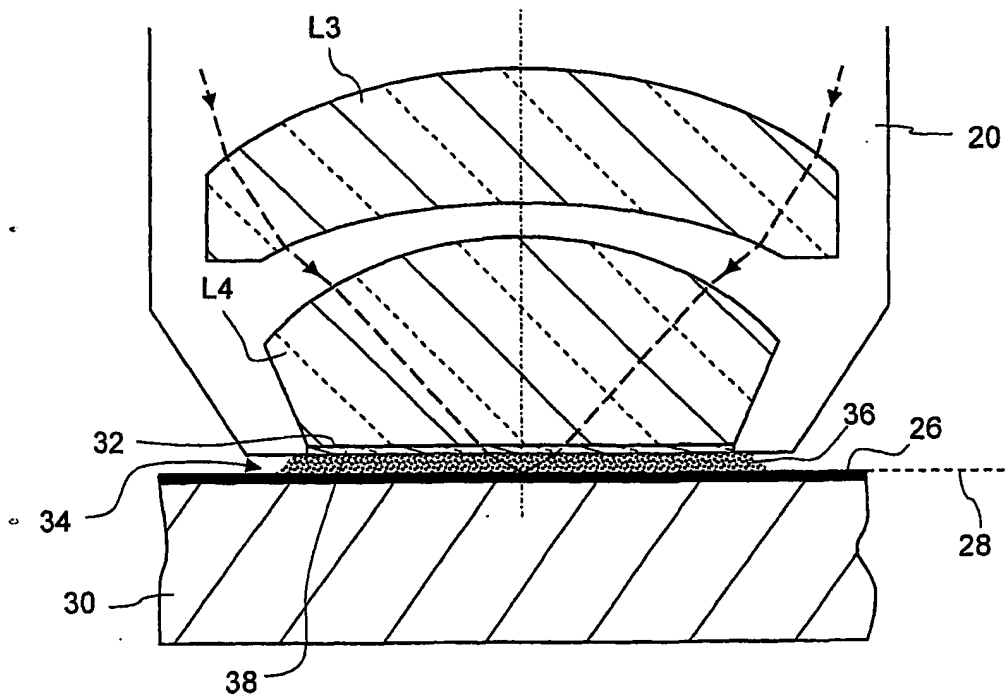
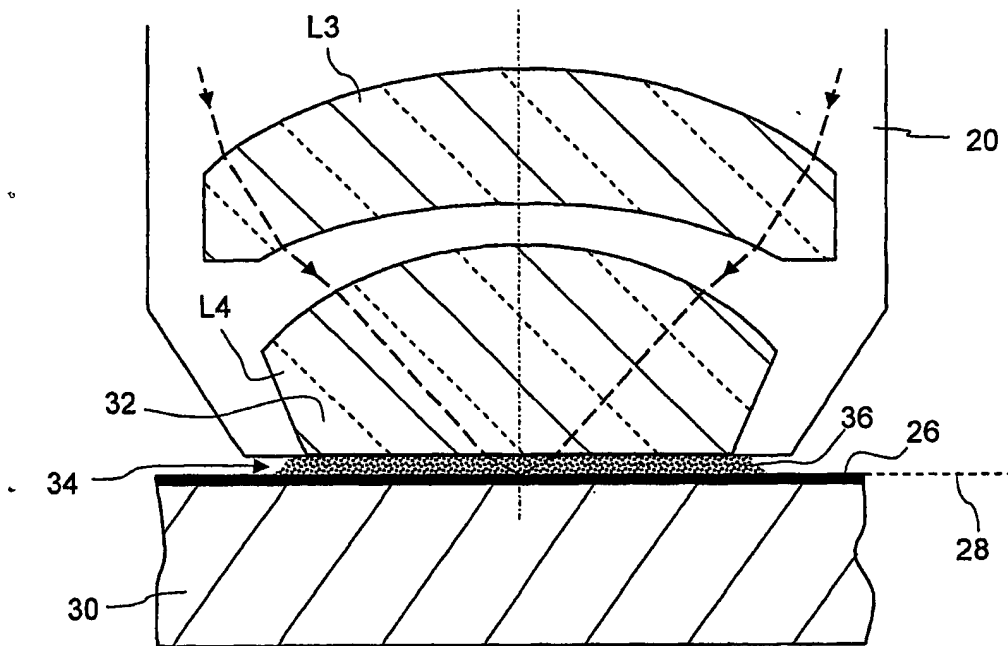


Fig. 1

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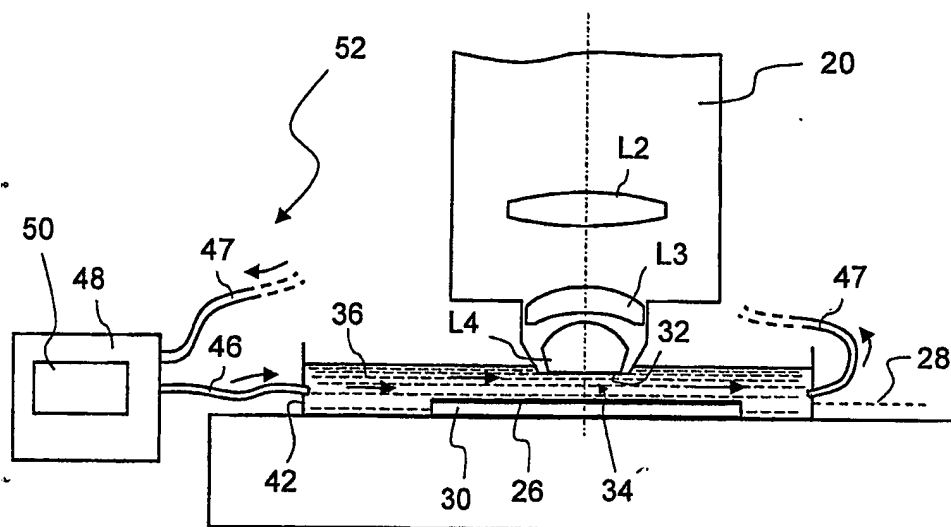


Fig. 4

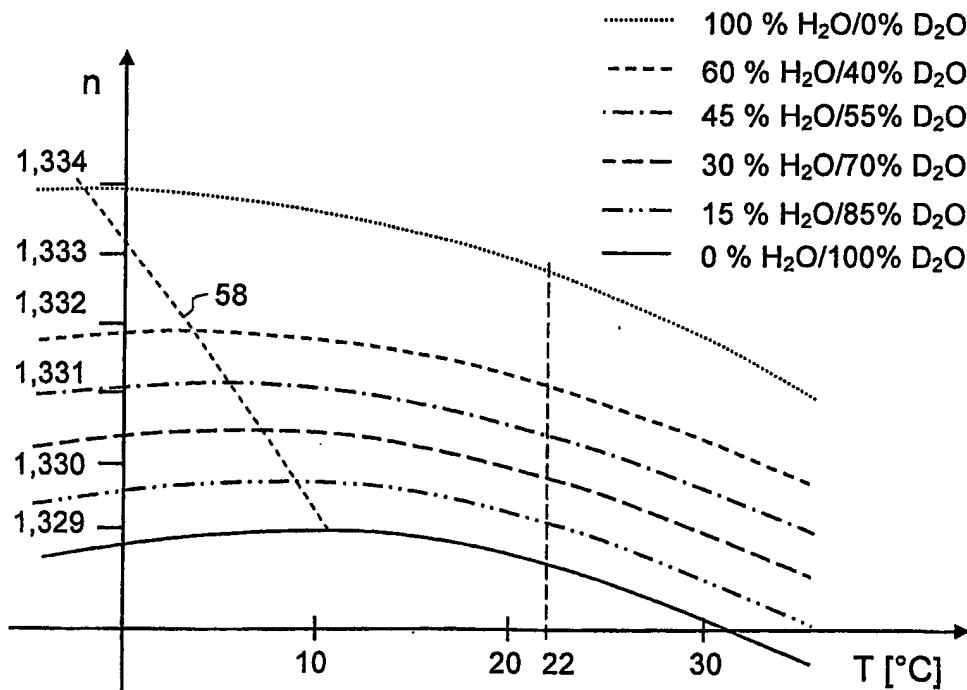


Fig. 5

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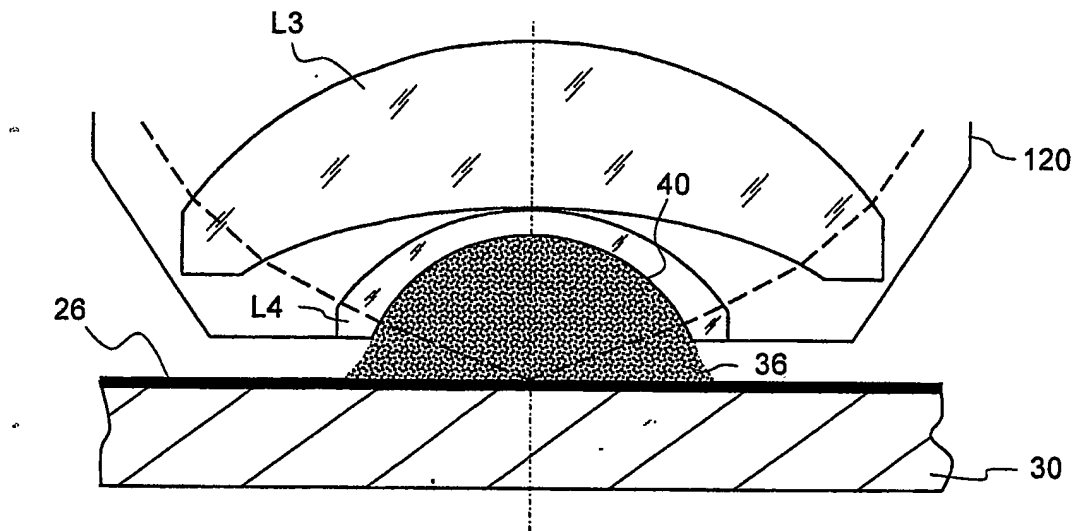


Fig. 6

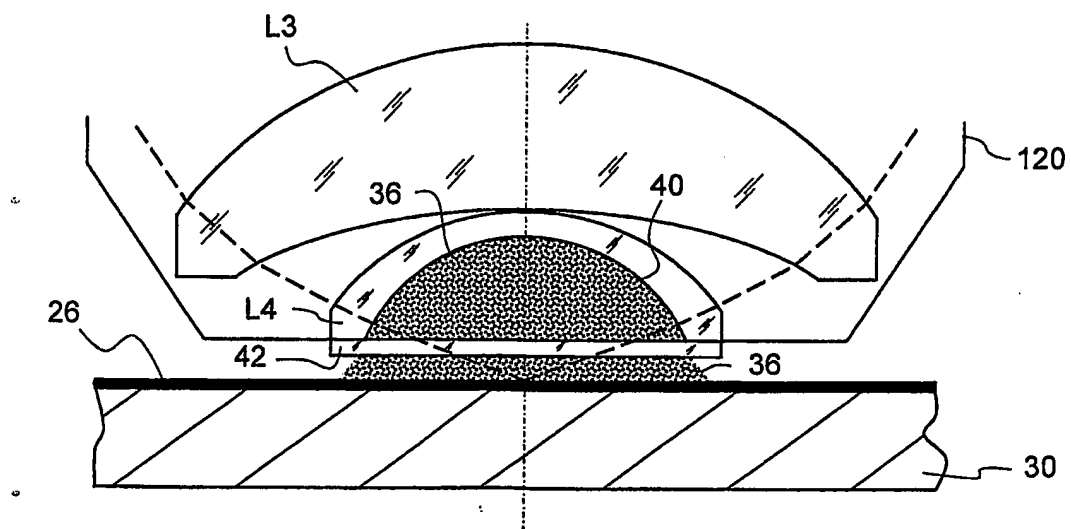


Fig. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/014728

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/174408 A1 (ROSTALSKI HANS-JUERGEN ET AL) 18 September 2003 (2003-09-18) paragraph [0057]	32,37
X	BRUCE SMITH: "Water-based 193nm immersion lithography" [Online] 28 January 2004 (2004-01-28), XP002330079 Retrieved from the Internet: URL: http://www.sematech.org/resources/litho/meetings/immersion/20040128/presentation%206%20RIT%20microstepper%20efforts_Smith.pdf [retrieved on 2005-05-30] page 13 - page 14 page 19 page 22	32,33

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

31 May 2005

Date of mailing of the international search report

25.08.2005

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/014728

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2005/006026 A (NIKON RESEARCH CORPORATION OF AMERICA; SOGARD, MICHAEL) 20 January 2005 (2005-01-20) paragraphs [0006], [0009] -----	1,3, 34-37
P,X	EP 1 486 827 A (ASML NETHERLANDS B.V) 15 December 2004 (2004-12-15) paragraph [0073] -----	33
E	EP 1 522 894 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 13 April 2005 (2005-04-13) paragraph [0070] -----	33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/014728

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

• see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
• 1-30, 32-37

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-30, 32-37

Prior art (US2003174408): projection exposure apparatus with particular projection lens design for immersion lithography

Special technical features:

immersion liquid enriched with heavy isotopes, immersion liquid supplemented with additives, immersion liquid with refraction index equal to refraction index of last optical element

Problem solved by these special technical features:
chemical reactivity of the immersion liquid

2. claim: 31

Special technical features: particular temperature dependency of the refractive index of the immersion liquid
Problem solved by these special technical features: imaging properties of projection lens are not altered by minor temperature fluctuations of the immersion liquid

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/014728

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003174408 A1	18-09-2003	DE 10210899 A1	18-09-2003
		AU 2002312872 A1	22-09-2003
		AU 2003221490 A1	22-09-2003
		WO 03077036 A1	18-09-2003
		WO 03077037 A1	18-09-2003
		EP 1483625 A1	08-12-2004
		EP 1485760 A1	15-12-2004
		JP 2005519347 T	30-06-2005
		JP 2005519348 T	30-06-2005
		US 2005030506 A1	10-02-2005
		US 2005141098 A1	30-06-2005
WO 2005006026 A	20-01-2005	WO 2005006026 A2	20-01-2005
EP 1486827 A	15-12-2004	EP 1489461 A1	22-12-2004
		EP 1486827 A2	15-12-2004
		JP 2005005713 A	06-01-2005
		US 2005024609 A1	03-02-2005
EP 1522894 A	13-04-2005	JP 2005136374 A	26-05-2005
		CN 1606128 A	13-04-2005
		EP 1522894 A2	13-04-2005
		US 2005074704 A1	07-04-2005